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STUDY OF THE CATHODE PROCESS DURING ELECTROREDUCTION OF OXALIC ACID

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Electrosynthesis of organic compounds has long interested investigators, but up to the present time has seldom had practical applications in suitable production activities. However, its annual number of published works is exceedingly high.

The many investigations and particularly the new American works show little interest in the theory or mechanism of electrode processes or even in the detailed analysis of all reaction products. Following the early classical works of Elbs and Haber on the electroreduction of nitrobenzene, are only a few through studies on the theory of electrode processes.

In this work, we attempt to contribute to the theory of the cathode process, by relating electrosynthesis behavior and ~~anodic~~ ^{cathodic} curves of current density versus cathode potential ~~anodic~~ ^{cathodic} polarization curves. The method of polarization curves still plays an important role in electrochemistry, especially for electro-metallurgical processes.

To solve this problem, we will use the electrode process, which has been thoroughly studied from the chemical standpoint, and compare the polarization curves with the behavior of the chemical transformations. To fulfill this aim, we consider the electroreduction of oxalic acid.

The electroreduction of oxalic acid is used in industry to produce glyoxalic acid $\text{HO}_2\text{C}\cdot\text{CHO}$, which is used to obtain vanillin and vanillin for the perfumery and confectionary industries.

Several methods of obtaining glyoxalic acid are described in literature. Tafel and Friedrichs (1) reduced oxalic acid on lead and mercury cathodes and noted the advantage of the mercury cathode, on which higher yields of glyoxalic acid were obtained. The reduction on the lead cathode was con-

- 1 -

CONFIDENTIAL

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ducted at 10° with a current of 4 amperes in 50 ml of 10 percent sulfuric acid, containing 10 grams of oxalic acid. The yield of glyoxalic acid in the first 30 minutes was equal to 100 percent with respect to the current and fell to 50 percent in the next 30 minutes; thereafter the yield quickly fell to 1.5 percent and continued to decrease slowly. Similar results have been obtained by several other authors.

During reaction, the catholyte is heated considerably by the current.. At temperatures of 40 degrees and higher, however, several observers found glycolic acid in the catholyte - a product of the further reduction of glyoxalic acid. In the reduction products Baur (2) discovered formaldehyde, which formed from the glyoxal by the ^{rupture}breaking of the carbon chain. Averi and Dales (3) described the reduction of oxalic acid on an iron cathode in an aqueous solution. In this process, the solution is heated to the boiling point and glycolic acid, $\text{HO}_2\text{C}\cdot\text{CH}_2\text{OH}$, is obtained. At present, the method with mercury and lead-amalgam cathodes is used in most cases to produce glyoxalic acid. There is also electrochemical production of glyoxalic acid in the Soviet Union.

By studying hydrogen overvoltage on mercury electrodes in various acid solutions, Gerasimenko discovered by the polarographic method the reduction of pure oxalic acid on Geyrovskiy's drop electrode.

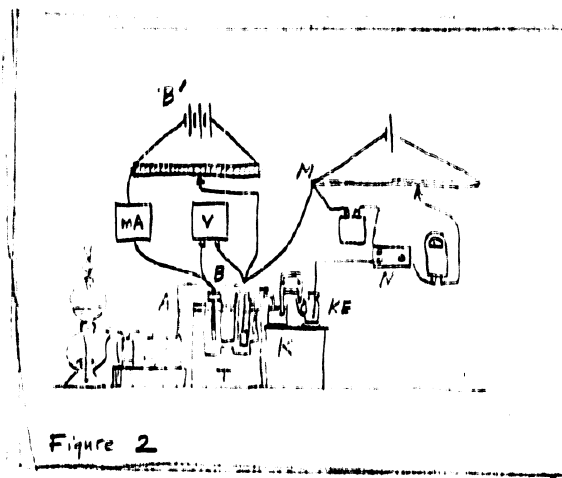
In connection with his theory of hydrogen overvoltage, he considered that the main process in the reduction is the reaction between a hypothetical negative ion H^- and the complex $\text{H}^+ (\text{C}_2\text{O}_4\text{H}_2)_4$, the existence of which, however, remains unproven.

Synthesis

Electrolytic reduction of oxalic acid on an amalgamated lead cathode was conducted under conditions approximating those used in production.

- 2 -

CONFIDENTIAL



NOTE: For the caption, see page 6, top.

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6. The process in the electrolyser and the shapes of the polarisation curves were correlated.

Bibliography

- (1) Ber., 37, 3189 (1904) - (2) Z. Elektroch., 25, 102 and ff. (1919)--
(3) Ber., 32, 2237 and ff. (1899) - (4) Z. Elektroch., 34, 128 and ff.
(1928) Submitted March 6, 1947.

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(Note: Figure 2 attached.)

CONFIDENTIAL

-12-

CONFIDENTIAL

overcharge or discharge of the separate polar groups of oxalic acid, as a result of which glyoxalic acid forms. This assumption, however, is still in need of additional proof.

Conclusions

1. The experimental investigation was conducted in order to study the process of electroreduction of oxalic acid to glyoxalic acid in the electrolyser. The shape of the polarisation curves was studied, since these also reflect the various stages of the cathode process.
2. The electro-reduction was carried out mainly on lead or lead-amalgam cathodes with various electrolyte concentrations (i.e., oxalic and sulfuric acid) and for various temperatures.
3. With the aid of indole and ferric chloride, qualitative reactions were made on glyoxalic and glycolic acids while electrolysis progressed in the electrolyser and while the polarisation curves were obtained.
4. It was established that when the first traces of glyoxalic acid appeared, a characteristic discontinuity or abrupt change in the path of the polarisation curves was observed for definite E 's and $i(D_K)$'s in "the region of unstable state". The given region appeared under all different conditions created although its configuration changed more or less, depending upon conditions.
5. When cathodes of platinum, copper, nickel, graphite and stainless steel were used for the same electrosynthesis no reduction products were discovered, and only hydrogen was liberated. In agreement with this, the polarisation curves for platinum, copper, and steel were of the form peculiar to the process of hydrogen liberation. The curve for nickel represented only a certain middle portion of the curve for hydrogen. In graphite some unexpected processes, not clear for the time being, ^{occurred} ~~occurred~~, as indicated by the positive values of all cathode potentials.

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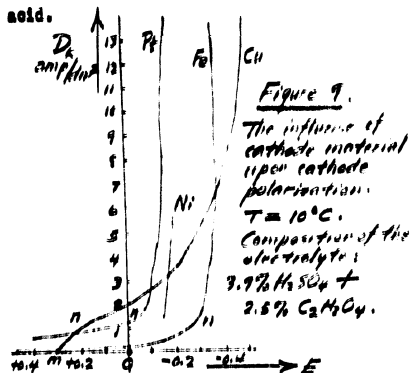
a lower $E = -0.05$ and also ended at $E = -0.5$, which is also lower than in the case of the lead cathode. Even at $E = -0.05$, the employment of indole revealed traces of glyoxalic acid.

Next, polarisation curves were obtained on cathodes of platinum, copper, nickel and stainless steel, which does not give glyoxalic acid (according to the literature and our verifying experiments). The corresponding curves are shown in Figure 9.

All of these are quite different from the curves for lead and its amalgam and suggest the simple curves obtained when determining potentials during the liberation of hydrogen and other gases, where depolarisers and secondary chemical processes do not exist.

These observations agree completely with the fact that reduction products on these cathodes are not been observed. It is true that on the initial segments of the curves ($m = n$), slight deviations from the smooth path are observed, but this can be explained by the influence of the adsorption on the metal of some traces of reduction products which were not revealed by the indicators.

The different effects in lead and lead-amalgam cathodes, on one hand, and on other electrodes, on the other hand, are possibly connected with the fact that the overvoltage ΔE is very high on the first electrodes in comparison with the latter ones. It is possible that the process of isolating hydrogen on the lead and mercury is much more difficult owing to the high ΔE and the cathode process expresses itself in this case in a slight



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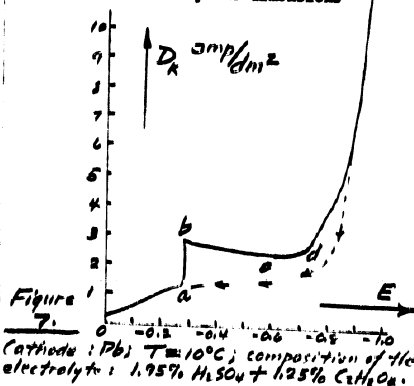
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Therefore, it might be assumed that either the glycolic acid emerges in quantities too small to be shown by the reaction, or that some other complicated process occurs.

The primary and main product, glyoxalic acid, is easily discovered in all cases by its reaction with indole even in the first minute of electrolysis in electrosynthesis (raspberry tint, sensitivity 1:1,000), and at the points b of the curves. When the concentration of oxalic or sulfuric acid is lowered, the characteristic peculiarities of the curves in "the region of instability" abed are maintained. Only the dimensions of b-c change slightly, as is shown in Figure 7.

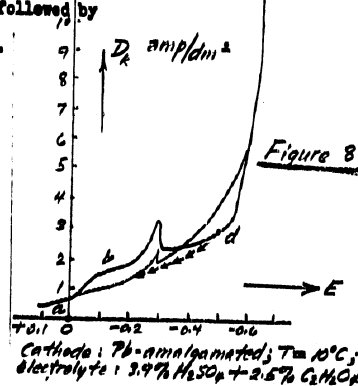
B. Electroreduction on Cathodes of Other Metals.

Since pure lead was used for the cathodes in all the preceding experiments in section A, we conducted experiments in the electrolyser to obtain polarisation curves for other metals.



For another example of a cathode on which glyoxalic acid was well synthesized, we took amalgamated lead and the fine reputation of this electrode was fully confirmed by our experiments. The lead was amalgamated by immersing the lead in mercurous nitrate followed by rinsing and rubbing with a clean cloth.

The curves obtained also revealed a "zone of instability," a b c d, with a general character suggestive of that for the lead cathode (Figure 8), the difference being only that the zone began at

- 9 -
CONFIDENTIAL

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the cathode or in the surface of the lead cathode itself, which was polished to a luster with emery paper (degassed with benzene before electrolysis and lost its luster during electrolysis).

To solve the problem, the following experiment were conducted. During the emergence of the ^{new} mentioned above, the cathode was quickly replaced by a new one, with the help of which further electrolysis was continued for the construction of the polarisation curves. This curve is shown in Figure 6, in which we note a more complex set of curves in the "region of unstable state". The point *s* denotes those values of E and D_k (and also current densities) at which the electrodes were changed).

According to the figure, starting from that point, the ^{behavior} ~~course~~ of curve 1 is altogether different from the initial shape of the curve and shows that the basic character of the process did not change toward simplification of the curve with the introduction of the new cathode; i.e., the unstable state was maintained. Analysis of the catholyte did not reveal lead in it, which indicates the absence of those interactions which would have been connected with its dissolving.

Most probable of all, therefore, is the assumption that the complex configuration of the curves is due to the appearance of new substances in the solution itself. It might be assumed that at the higher temperature, that is at 40° , glycolic acid emerged, i.e., a product of further reduction. However, the qualitative reaction with the ferric chloride solution did not yield the corresponding color (a deep yellow tint).

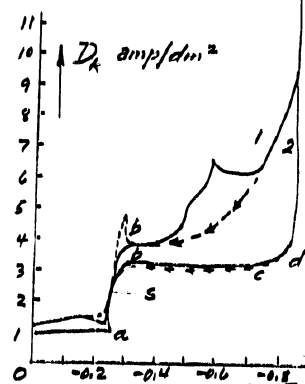


Figure 6. Cathode: Pb; $T = 40^\circ\text{C}$;

- 8 - composition of electrolyte: 2.9% H_2SO_4 + 2.5% $\text{C}_2\text{H}_2\text{O}_4$.

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A continuous rise of the curve without points of inflection up to $d = 20 \frac{\text{amp}}{\text{dm}^2}$ follows; higher current densities were not used.

The solid curve in Figure 4 shows the cathode process for a lower temperature ($9-10^\circ$). This produces a picture which is for the most part identical with that shown in Figure 3, as there are sectors on both, noted by the letters a, b, c, d. There are only slight deviations in the dimensions of these characteristics sections. The dotted line (the return path) gives a rather blurred picture of the behavior of this process.

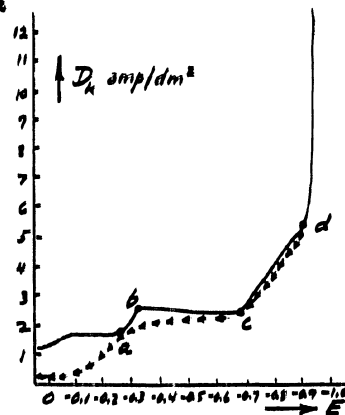


Figure 4. Cathode: Pb.
 $T = 9^\circ\text{C}$.
Composition of electrolyte:
 $3.0\% \text{H}_2\text{SO}_4 + 2.5\% \text{C}_6\text{H}_6\text{O}_4$.

From Figure 5, the picture of the phenomena becomes complicated at 40° . This curve also has the point a, but at b, also for -0.3 volts, appears a sharp peak after which the curve falls to a minimum c and then rises smoothly. The emergence of the peak, corresponding to a certain "region of unstable state," apparently must be explained by some abrupt change either in the solution around

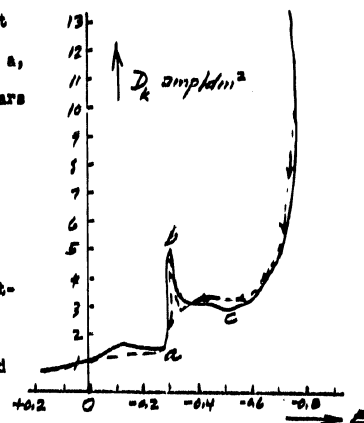


Figure 5. Cathode: Pb; $T = 40^\circ\text{C}$; composition of electrolyte: $3.9\% \text{H}_2\text{SO}_4 + 2.5\% \text{C}_6\text{H}_6\text{O}_4$.

- 7 -

CONFIDENTIAL

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Discontinuities in the curves for lead cathodes forces one to assume the existence of complex electroreduction processes and perhaps several chemical reactions. Upon raising the cathode potential to -0.3 volt, one observes a fairly substantial upward jump in current density on all curves. But the rise in current density was of short duration, \leftarrow

Figure 2 - Plan of arrangement for recording polarization curves - Reproduces drawing on p. 340

of this translation
K-cathode, A-anode (graphite), B-tube for hydrogen which stirs catholyte, T-thermostat, KF-calomel semicell (saturated), E'-direct current supply, M and N-potentiometer terminals. *and later a slight drop in current density was again observed. In a short segment of the curve showing a rise in cathode potential (approximately from 0.3 to 0.7-0.8 volts), instability in the curves was noted.*

Let us make a few observations concerning the characteristics of the following curves selected as representative of the various groups of curves. The curves shown by solid lines represent observations under rising cathode potentials (forward or increasing *behavior* *course*), and dotted lines represent the successive drop of potentials on the abscissa (return or decreasing behavior).

Figure 3 shows that the curve at first rises more or less smoothly and then $i(D_K)$ jumps abruptly around $E = -0.3$ volt between points a and b, *which* after the curve is almost parallel with the abscissa in the *follows* sector b-c; and then a sharp ascent of the curve, slightly complicated by the bend at d.

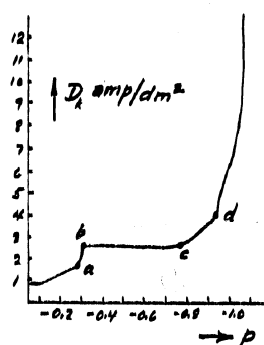


Figure 3. Cathode: Pb.
 $T = 18^\circ C.$
Composition of electrolyte:
3.9% H_2SO_4 + 2.5% $C_6H_6O_4$.

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CONFIDENTIAL

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The presence of glycolic acid, which under certain conditions emerges during electrolysis, was not discovered under the conditions of our synthesis (with the aid of ferric chloride, which should react with it to produce a deep yellow tint). Glycolic acid was not observed when the catholyte was heated to 40° or even 90°. Very similar results were obtained on pure lead.

Study of the Cathode Process by the Method of Polarisation Curves.

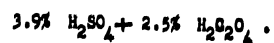
The following factors which influence the cathode process were studied:

- 1) effect of cathode material.
- 2) effect of temperatures (10°, 20°, and 40°).
- 3) effect of oxalic and sulfuric acid concentration.

To determine the role of cathode material, polarisation curves were obtained for lead cathode and amalgamated lead and also for copper, graphite, nickel, and iron electrodes and stainless steel cathodes. We studied the various electrodes, although the literature notes only the feasibility of pure and amalgamated lead and also of the mercury cathode.

A. A Study of Polarisation Curves Obtained for a Lead Cathode

An electrolyte of the following composition was used to obtain the polarisation curves:



The catholyte was mixed with the aid of hydrogen bubbles, uniformly distributed through the solution. The plan showing the arrangement of equipment for obtaining the curves is shown in Figure 2.

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The glyoxalic acid obtained is determined by introducing into catholyte sample fixed quantities of bisulfite followed by titration with iodine of bisulfite, which is not combined with this acid.

Table 1 gives data on the solubility of oxalic acid. Table 2 shows the time behavior of the catholyte during electrolysis.

Table 2

No. of hours from start of experiment	No. of milliliters of catholyte taken for analysis.	No. milliliters of NaHSO_3 $n = 1.285$	No. of milliliters of I_2 $n = 1.07$	No. of milliliters of glyoxalic acid developing	Output of glyoxalic acid with respect to current
1	2	7.71	5.67	2.04 ml 1.48 grams	
2	2	5.14	3.10	2.04 ml 1.48 grams	
3	2	5.14	2.46	2.679 ml	
4	2	5.14	2.46	2.68 ml	
5	2	5.14	2.15	3.00 ml 2.22 grams	
6	2	5.14	1.5	2.36 grams	8.1%
7	2	5.14	1.82	2.36 grams	5.62%
8	2	5.14	1.82		5.4%

Glyoxalic acid appears in the first minute of electrolysis, as can be shown with indole, with which it gives a raspberry tint in concentrated sulfuric acid (sensitivity of reaction 1:1000). The amount of glyoxalic acid increases for five hours and then remains almost unchanged during further electrolysis.

- 4 -

CONFIDENTIAL

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NOTE: All figures can be put last.

A chemical 1.5-liter breaker served as the electrolyser; a lead cylinder is the anode (A -Fig 1). The anode field is separated from that of the cathode by a ceramic diaphragm (D). The cathode is an amalgamated lead plate with a surface area of 0.85 square decimeter. The catholyte is stirred by a glass agitator (M). The electrolyser is cooled externally by a mixture of ice and salt. The catholyte is additionally cooled by cold water, admitted through a glass coil under the cathode. Thus, the temperature of the catholyte is held at 10°, which is the best for synthesis.

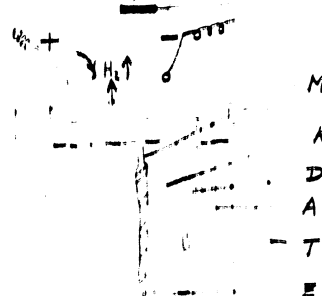


Fig 1-Diagram of electrolyser for reduction of oxalic acid.
K-cathode A-anode
D-diaphragm M-agitator
T-thermostat
Z-cooling coil
Reproduce drawing on p.238 of text.

The composition of the anolyte is 11 percent H_2SO_4 (volume 500 mm). The initial composition of the catholyte is 3.9 percent H_2SO_4 (volume 200 mm.) The aqueous oxalic acid $H_2C_2O_4 \cdot 2H_2O$ has an initial concentration of 2.5 percent. The voltage on the electrolyser is 7.5 volts. The current is 2 amperes. The cathode current density is 2.35 amperes per square decimeter.

Table 1

Solubility of oxalic acid in grams/liter

Temperature	$C_2H_2O_4$	$C_2H_2O_4 \cdot 2H_2O$
0°	3.6	5.2
10°	5.3	8.0
20°	10.2	13.9
40°	22.8	35.0

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